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THE REACTIONS OF SOME ORGANOTIN(IV) CHLORIDES WITH ANTIMONY(V) CHLORIDE AND BORON(III) CHLORIDE

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Abstract—The reactions of the organotin chlorides R_nSnCl_{4-n}($R = Me$ or Ph; $0 \leqslant n \leqslant 4$) with the Lewis acids $SbCl_5$ and BCl_3 have been investigated by ^{119}Sn and (where appropriate) ^{11}B NMR spectroscopy. The results show that transfer of organo-groups to antimony or boron usually takes place rather than chloride abstraction to give cationic tin(IV) species, and this process is more facile for phenyl than methyl groups. These conclusions have been confirmed in some instances by isolation of the non-volatile reaction products.

The reactions of strong Lewis acids such as antimony(V) chloride, boron trichloride or aluminium trichloride with chloroorgano-derivatives of some main group elements including phosphorus(V)[1] and arsenic(V)[2] have been used to prepare cationic derivatives, eqns (1) and (2), which could then be identified by spectroscopic techniques as well as by elemental analysis of the isolated products.

$$R_nPCl_{5-n} + SbCl_5 \rightarrow [R_nPCl_{4-n}]^+ SbCl_6^- \quad (1)$$

$$R_nAsCl_{5-n} + BCl_3 \rightarrow [R_nAsCl_{4-n}]^+ BCl_4^-. \quad (2)$$

In certain instances, however, $SbCl_5$ is capable of undergoing exchange reactions with organometallic compounds, resulting in the formation of organoantimony(V) chlorides. Thus the preparation of Ph_2SbCl_3 has been described by reaction of Ph_4Pb with $SbCl_5$.[3] Organoboron halides are also well-established, and ^{11}B NMR shifts have been reported for the phenyl and methyl compounds.[4–7] The reaction of Ph_4Sn with BCl_3 in various solvents has been used to prepare $PhBCl_2$,[8] but the tin-containing product varied with the solvent. $PhSnCl_3$ was identified in the residues from reaction in CH_2Cl_2, but $SnCl_4$ was found in CCl_4 or in the absence of a solvent.[8] Similarly the methyl boron bromides have been prepared by reaction of Me_4Sn with BBr_3,[9] but in contrast with the phenyl system not more than two of the alkyl groups could be transferred from tin to boron, and the tin-containing product was found to be Me_2SnBr_2. It was therefore of considerable interest to investigate the reactions of organotin(IV) chlorides with $SbCl_5$ and BCl_3, using ^{119}Sn NMR spectroscopy to identify the main tin-containing species present in solution. Formation of a cationic three-coordinate tin(IV) species was expected to cause a large downfield shift of the ^{119}Sn resonance from the position of the starting material,[10,11] while the occurrence of exchange reactions should also be observable. In the case of BCl_3, ^{11}B NMR spectroscopy could also be used to follow the progress of the reactions. The results obtained have been confirmed in some instances by isolation and analysis of the non-volatile reaction products.

EXPERIMENTAL

All manipulations including NMR sample preparation were carried out in an inert atmosphere of dry nitrogen. Chemicals of the best available commercial grade were used, in general without further purification. For reactions with $SbCl_5$, the organotin compound was usually dissolved in CH_2Cl_2 and the requisite amount of $SbCl_5$ diluted with the same solvent was added. The non-volatile products were isolated as required by removing CH_2Cl_2 and any excess $SbCl_5$ *in vacuo*, adding a small amount of low-boiling petroleum ether, and again pumping *in vacuo* to remove the last traces of solvent. Some reactions were carried out with neat $SbCl_5$, as described in the Results section, by cautiously adding $SbCl_5$ dropwise to the organotin compound in an NMR tube. The exothermic reactions which resulted were allowed to subside before the ^{119}Sn NMR spectra of the resultant clear solutions were recorded.

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For reactions with BCl_3, a preweighed amount of the tin(IV) compound was dissolved in CH_2Cl_2 in a thick-walled NMR tube of 8.4 mm outside diameter, which was connected to the vacuum line via a modified socket joint. This section of the line was isolated, and the required amount of BCl_3 condensed into a graduated cold finger attached to the line at 77K. The NMR tube was then cooled to 77K while the cold finger was allowed to warm up slowly to room temperature, resulting in the condensation of BCl_3 into the NMR tube. When this process was complete, the tube was sealed, and allowed to warm up gradually to room temperature.

^{119}Sn NMR spectra were recorded at 307.2K on a Fourier transform multinuclear spectrometer constructed by Dr. A. Royston, which utilises the permanent magnet (1.4T) from a Perkin–Elmer R10 spectrometer, a Racal 9061/2 frequency synthesiser as the frequency source, a Dec pdp 11/34 computer, and a HIPLOT digital plotter. Samples were contained in 8.4 mm o.d. stationary sample tubes. Chemical shifts were measured relative to external Me_4Sn, with the downfield direction taken as positive. ^{11}B spectra were similarly obtained relative to external $(MeO)_3B$. IR spectra between 650 and 250 cm^{-1} were recorded on a Perkin–Elmer 457 instrument. C, H and Cl microanalyses were determined as described previously,[12] and Sn and Sb microanalyses by atomic absorption spectroscopy.

RESULTS AND DISCUSSION

(a) *Reactions with antimony(V) chloride*

Initially reactions were carried out in CH_2Cl_2 as solvent by adding slightly more than an equimolar amount of $SbCl_5$ to the organotin species R_nSnCl_{4-n} (R = Me or Ph; $0 \leq n \leq 4$). When reaction had subsided the ^{119}Sn NMR spectra of samples of the resultant solutions were recorded; the results are given in Table 1, together with literature values for the chemical shifts of the starting materials in this solvent where available.[10,11] Chemical shifts of four-coordinate tin compounds are known to be markedly concentration- and solvent-dependent,[11] and the species formed could be readily identified when this was taken into account, as shown in Table 1. There was no evidence for formation of cationic tin(IV) species, but transfer of organo-groups to antimony(V) appeared to occur with all the phenyltin compounds and with Me_4Sn and Me_3SnCl, whereas Me_2SnCl_2, $MeSnCl_3$ and $SnCl_4$ did not react under these conditions. (Me_2SnCl_2 reacted with an excess of $SbCl_5$ to give $MeSnCl_3$, although some starting material was still present.) The reactions were repeated (except for $SnCl_4$) using a larger excess of $SbCl_5$, and the non-volatile products were isolated after any effervescence had subsided (Experimental section). The results of ^{119}Sn NMR investigations and elemental analyses of the products are shown in Table 2, and indicate that under these more forcing conditions Me_2SnCl_2 also transfers one methyl

Table 1. $\delta^{119}Sn$ (ppm) for reaction of some organotin chlorides with $SbCl_5$ in CH_2Cl_2

Compound	δ ^{119}Sn (p.p.m.) in CH_2Cl_2 [11]	δ ^{119}Sn (p.p.m.) after reaction with $SbCl_5$	Assignment
Ph_4Sn	-140[a]	-29.7	Ph_2SnCl_2
Ph_3SnCl	-48	-62.9	$PhSnCl_3$
Ph_2SnCl_2	-32	-62.8	$PhSnCl_3$
		-162.3[b]	$SnCl_4$
$PhSnCl_3$	-63	-150.1	$SnCl_4$
$SnCl_4$	-150	-150.1	$SnCl_4$
Me_4Sn	0	171.3	Me_3SnCl
		131.7[b]	Me_2SnCl_2
Me_3SnCl	155 to 169	143.2	Me_2SnCl_2
Me_2SnCl_2	137	139.6	Me_2SnCl_2
$MeSnCl_3$	21[c]	17.5	$MeSnCl_3$

a estimated value

b major peak

c $CHCl_3$ solvent

Table 2. Products isolated from reactions with $SbCl_5$

Starting material	Product Appearance	$\delta^{119}Sn$ (p.p.m.)	Product	Analysis found (%)	Analysis required (%)
Me_4Sn	white powdery solid	130.3[a]	Me_2SnCl_2 + Me_2SbCl_3 (1:1)	Sn, 22.7; Sb, 25.9; Cl, 35.2; C, 10.8; H, 3.3.	Sn, 24.9; Sb, 25.5; Cl, 37.1; C, 10.0; H, 2.5.
Me_3SnCl	a) off-white crystals	132.6[b]	Me_2SnCl_2 Me_2SbCl_3 (2:1)	Sn, 33.3; Sb, 16.7; Cl, 33.7; C, 10.3; H, 2.9.	Sn, 34.1; Sb, 17.5; Cl, 35.7; C, 10.3; H, 2.6.
	b) orange-red crystals	235.1[b]	see text	Sn, 35.7; Sb, 16.1; Cl, 35.3; C, 9.2; H, 2.8	
Me_2SnCl_2	red liquid	14.0[b]	$MeSnCl_3$		
$MeSnCl_3$	red liquid	17.5[b]	$MeSnCl_3$		
Ph_4Sn	white solid	-	Ph_2SbCl_3	Sn, -; Sb, 28.7; Cl, 26.7; C, 37.5; H, 2.6.	Sn, -; Sb, 31.9; Cl, 27.8; C, 37.6; H, 2.6.
Ph_3SnCl	off-white solid	-	Ph_2SbCl_3	Sn, -; Sb, 32.0; Cl, 29.7; C, 37.3; H, 2.6.	Sn, -; Sb, 31.9; Cl, 27.8; C, 37.6; H, 2.6.
Ph_2SnCl_2	off-white solid	-	Ph_2SbCl_3	Sn, -; Sb, 29.5; Cl, 26.9; C, 35.9; H, 3.0.	Sn, -; Sb, 31.9; Cl, 27.8; C, 37.6; H, 2.6.
$PhSnCl_3$	grey solid	-	$PhSbCl_4$	Sn, -; Sb, 35.1; Cl, 41.6; C, 21.1; H, 1.5.	Sn, -; Sb, 35.8; Cl, 41.6; C, 21.1; H, 1.5.

[a] CH_2Cl_2 solvent. [b] Solid state or neat liquid

group to antimony but $MeSnCl_3$ does not react. No tin was detected in any of the products isolated from reaction of the phenyltin compounds, and these appear to be converted completely to $SnCl_4$, which is then removed with the volatiles. The elemental analyses confirm that the non-volatile product is Ph_2SbCl_3 from Ph_4Sn, Ph_3SnCl and Ph_2SnCl_2, and $PhSbCl_4$ from $PhSnCl_3$. The reaction of $SbCl_5$ with Ph_4Sn thus parallels that with Ph_4Pb.[3] The IR spectra of the products from Ph_4Sn, Ph_3SnCl and Ph_2SnCl_2 were also virtually identical, and differed from that of the reaction product with $PhSnCl_3$, as expected. These reactions may indeed provide a useful route for preparation of the phenylantimony chlorides. The white or off-white products from the Me_4Sn and Me_3SnCl reactions were readily identified as 1:1 and 2:1 mixtures of Me_2SnCl_2 and Me_2SbCl_3 respectively, eqns (3) and (4), and may similarly be suitable for preparation of Me_2SbCl_3.

$$Me_4Sn + SbCl_5 \rightarrow Me_2SnCl_2 + Me_2SbCl_3 \qquad (3)$$

$$2Me_3SnCl + SbCl_5 \rightarrow 2Me_2SnCl_2 + Me_2SbCl_3. \qquad (4)$$

In one reaction of Me_3SnCl with $SbCl_5$, however, a crystalline product was obtained which gave a solid state signal at very low field (Table 2), as expected for a three-coordinate cationic species. Nevertheless the analysis of the solid was similar to that of the "normal' product, as shown, and the experiment was not reproducible. Assignment of this signal to a cationic tin(IV) species such as Me_3Sn^+ is thus very tentative, but is supported by some of the results from reactions of Me_4Sn with neat $SbCl_5$, described below. Me_2SnCl_2 and $MeSnCl_3$ both gave liquid products, the ^{119}Sn NMR of which indicated the presence of $MeSnCl_3$ as the only tin-containing species. These liquids were not analysed.

Similar reactions were also carried out with neat $SbCl_5$, as indicated previously. A single ^{119}Sn NMR signal was obtained in most cases from the resultant solutions (Table 3), and the species formed could then be readily identified. Me_3SnCl and Me_2SnCl_2 both appear to lose one methyl group under these conditions while $MeSnCl_3$ and $SnCl_4$ do not react. All the phenyltin compounds form $SnCl_4$ exclusively, however, in agreement with the results from excess $SbCl_5$ in CH_2Cl_2. No attempt was made to isolate the products from these

Table 3. δ ^{119}Sn (ppm) of some organotin chlorides in neat $SbCl_5$

Starting Material	δ ^{119}Sn (p.p.m.)	Assignment
Me_3SnCl	137.4	Me_2SnCl_2
Me_2SnCl_2	20.9	$MeSnCl_3$
$MeSnCl_3$	21.0	$MeSnCl_3$
$SnCl_4$	-150.1	$SnCl_4$
Ph_4Sn	-150.1	$SnCl_4$
Ph_3SnCl	-150.1	$SnCl_4$
Ph_2SnCl_2	-153.6	$SnCl_4$
$PhSnCl_3$	-150.1	$SnCl_4$

reactions since the NMR data appeared quite conclusive.

The most unusual results were obtained from Me_4Sn, where the shifts ascribed to the tri- and dimethyltin species which form the reaction products differed markedly with the relative concentrations of the reagents (Table 4). When a large excess of Me_4Sn was used, the signals were at 160.6 (Me_3SnCl), 97.8 and 0.0 (Me_4Sn) ppm. A 2:1 molar ratio of Me_4Sn to $SbCl_5$ similarly gave resonances at 160.6, 104.7 and 0.0 ppm. A 1:1 ratio of reagents led to peaks at 208.0, 131.2 (Me_2SnCl_2) and -5.0 ppm. Other solutions with an excess of Me_4Sn, but where this was not measured quantitatively, gave signals in positions intermediate between those for the 1:1 and 2:1 mixtures, as shown, while an excess of $SbCl_5$ yielded only one strong signal at 136.4 ppm, readily assigned to Me_2SnCl_2. Thus the resonance for Me_3SnCl has a normal shift value when excess Me_4Sn ($\geqslant$2:1) is present, but moves progressively to lower field and decreases in intensity as the Sn:Sb ratio falls. The downfield movement could be due to partial ionisation, facilitated by the increasing concentration of $SbCl_5$, eqn (5),

$$Me_3SnCl + SbCl_5 \rightleftharpoons Me_3Sn^+SbCl_6^- \qquad (5)$$

with rapid exchange on the NMR time scale between the covalent and ionic tin(IV) species.

The more difficult data to explain are those for the dimethyltin derivatives, since the shift is initially to higher field of the normal position, which is only reached at Sn:Sb ratios of 1:1 or less. Association of Me_2SnCl_2 molecules might increase the shielding about each tin nucleus and thus cause an upfield shift, but aggregation would seem to be more likely at higher concentrations of Me_2SnCl_2, the opposite trend to that observed. Me_2SnCl_2 is known to be associated in the solid state, with a distorted octahedral arrangement about each tin atom and asymmetric chlorine bridges in a linear chain polymer.[13] Me_3SnCl is also polymeric at 135K, with five-coordinate tin and an asymmetric chlorine bridge, but the intermolecular association is apparently disrupted by melting or dissolution in CS_2.[14] An alternative possibility is the formation of octahedral aggregates between $SbCl_5$ and Me_2SnCl_2 such as $Cl_4SbCl_2Me_2SnCl_2SbCl_4$, but formation of such species would appear more likely at high rather than low $SbCl_5$ concentrations. In any event there seems no reason to postulate ionisation of dimethyltin species, since no shifts downfield from the values in organic solvents[10,11] were found.

Table 4. δ ^{119}Sn (ppm) for reaction products from Me_4Sn and $SbCl_5$

Molar Ratio Me_4Sn: $SbCl_5$	δ ^{119}Sn (p.p.m.)		
	Me_3SnCl	Me_2SnCl_2	Me_4Sn
Large xs Me_4Sn	160.6*	97.8	0.0
2:1	160.6*	104.7	0.0
xs Me_4Sn^a	172.8*	113.5	not recorded
xs Me_4Sn^a	179.2*	117.7	not recorded
xs Me_4Sn^a	186.8	124.0*	not recorded
1:1	208.0	131.2*	-5.0
xs $SbCl_5$		136.4*	

* major peak   a not measured quantitatively

(b) *Reactions with boron trichloride*

The solutions were prepared as described in the Experimental section and their ^{119}Sn and ^{11}B NMR spectra were recorded. The results are shown in Table 5, and indicate that organogroup transfer rather than chloride abstraction again takes place. Since BCl_3 is a weaker Lewis acid than $SbCl_5$, and R_4Sn compounds have been used to prepare organoboron derivatives,[8,9] this behaviour is not unexpected. Interpretation of the results for the methyltin compounds is quite straightforward and the ^{11}B NMR shifts for $MeBCl_2$ and Me_2BCl, where formed, are in good agreement with literature data.[7] Reaction between an excess of Me_4Sn and BCl_3 was also carried out to see whether Me_3B (δ ^{11}B 68.9 ppm[7]) would be formed. The ^{11}B spectrum contained no BCl_3 resonance, showing that it had reacted completely. The major peak present was due to $MeBCl_2$, with a smaller signal from Me_2BCl, and there was no evidence for formation of Me_3B. Me_2SnCl_2 and $MeSnCl_3$ did not react under these conditions, even with excess BCl_3.

The results for the phenyltin compounds require more discussion. A small peak at 13.4 ppm was seen in the ^{11}B NMR spectrum from reaction of Ph_4Sn with excess BCl_3, which cannot be ascribed to any of the phenylboron chlorides.[7] The shift is quite close to that reported for $PhB(OH)_2$[4], which could have been formed if a leakage of air or moisture into the tube had occurred, but no hydrolysis products of BCl_3 were detected. This signal was not present when a higher proportion of Ph_4Sn was used, but a broad hump at 38.7 ppm was apparent, intermediate in shift between $PhBCl_2$ (37.7 ppm) and Ph_2BCl (43.0 ppm).[7] Since an exchanging system between $PhBCl_2$ and Ph_2BCl is unlikely, this hump is presumably a composite with contributions from both species and overlapping peaks. A similar signal was observed in the ^{11}B spectrum from the reaction of Ph_2SnCl_2 with excess

Table 5. ^{119}Sn and ^{11}B shifts of products from reactions between organotin chlorides and BCl_3

System	δ ^{119}Sn (p.p.m.)	Tin-Containing product	δ ^{11}B (p.p.m.)	Boron-Containing product
Me_4Sn + excess BCl_3^{a}	146.7	Me_2SnCl_2	29.6*	BCl_3
			45.8	$MeBCl_2$
Me_4Sn + BCl_3 (~ 1.1)	140.5	Me_2SnCl_2	45.8*	$MeBCl_2$
			60.5	Me_2BCl
Me_3SnCl + BCl_3 $(\geqslant 1:0.7)$	167.2*	Me_3SnCl	44.1	$MeBCl_2$
	128.7	Me_2SnCl_2	59.3*	Me_2BCl
Me_2SnCl_2 + excess BCl_3^{a}	142.0	Me_2SnCl_2	29.4	BCl_3
$MeSnCl_3$ + excess BCl_3^{a}	19.8	$MeSnCl_3$	28.6	BCl_3
Ph_4Sn + excess BCl_3^{a}	-64.0	$PhSnCl_3$	13.4	See text
			29.4	BCl_3
			38.3*	$PhBCl_2$
Ph_4Sn + BCl_3 $(\sim 1:2)$	-62.7	$PhSnCl_3$	38.7	$PhBCl_2/Ph_2BCl$
Ph_3SnCl + excess BCl_3^{a}	-153.7	$SnCl_4$	29.6	BCl_3
			37.7*	$PhBCl_2$
Ph_2SnCl_2 + excess BCl_3^{a}	-62.9	$PhSnCl_3$	29.6	BCl_3
			39.4*	$PhBCl_2/Ph_2BCl$
$PhSnCl_3$ + excess BCl_3^{a}	-146.6	$SnCl_4$	28.6	BCl_3
			37.7*	$PhBCl_2$

* major peak

a Excess BCl_3 means > 1:1 molar ratio

of BCl_3. The other unexpected feature was that the reactions of Ph_4Sn with BCl_3 ($\sim 1:2$), and Ph_2SnCl_2 with excess BCl_3, both showed $PhSnCl_3$ as the tin-containing product, even though $PhSnCl_3$ (and Ph_3SnCl) clearly react with excess BCl_3 to form $SnCl_4$. This result is in agreement with the previous report of $PhSnCl_3$ as the reaction product from Ph_4Sn and BCl_3 in CH_2Cl_2.[8] The reactions are probably still continuing but at a slow rate, and the products observed ($PhSnCl_3$ or $SnCl_4$) may well depend on the relative concentrations of BCl_3 and the organotin compound, as well as the solvent. The ultimate product is presumably $SnCl_4$ in each case, corresponding to the reactions of the phenyltin compounds with $SbCl_5$ under forcing conditions.

It is thus evident that both $SbCl_5$ and BCl_3 usually react with the organotin compounds R_nSnCl_{4-n} (R = Me or Ph; $0 \leqslant n \leqslant 4$) to give organoantimony- and -boron-derivatives respectively, rather than cations by halogen abstraction. The only evidence for formation of cationic species is from systems with Me_3SnCl and $SbCl_5$ present. The exchange of phenyl groups is more facile than that of methyl groups, and $MeSnCl_3$ does not react with either reagent, even under forcing conditions. Me_2SnCl_2 similarly does not react with BCl_3, or with $SbCl_5$ in a 1:1 ratio in CH_2Cl_2, but does form $MeSnCl_3$ when excess $SbCl_5$ is used. The reactions with $SbCl_5$ may provide a useful preparative route to $PhSbCl_4$ and Ph_2SbCl_3, which have been isolated successfully, and possibly to Me_2SbCl_3 also.

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